

REMARKS

Claims 1-10 are pending in this application.

Applicants respectfully request reconsideration of the rejection of claims 1-3 and 5-10 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent Application Publication No. US 2003/0228120 A1 to *Kuramoto et al.* in view of U.S. Patent No. 3,809,732 to *Chandross et al.* As explained in the Amendment dated December 29, 2004, and for the additional reasons set forth below, the combination of *Kuramoto et al.* in view of *Chandross et al.* does not raise a *prima facie* case of obviousness against the subject matter defined in claims 1-3 and 5-10.

In the method for manufacturing a planar optical waveguide defined in claim 1, organic-inorganic materials are used as a core in the optical waveguide and light is irradiated onto the core, which increases the refractive index of the core. In support of the obviousness rejection, the Examiner alleges, among other things, that the *Chandross et al.* reference teaches a photolocking technology using pure organic polymers as core materials and the claimed method also uses a photopolymerization reaction between the organic part of the matrix and the photochemical monomers. Applicants respectfully submit that the Examiner's application of the *Chandross et al.* reference is improper because it fails to reflect the material features of organic-inorganic hybrid materials.

In the case of irradiating light onto organic-inorganic hybrid materials, it is impossible to explain fully the phenomenon of increasing refractive indices by photopolymerization reaction between photochemical monomers and the organic part of organic-inorganic hybrid materials. That means that other reactions (not disclosed in Applicants' specification) are involved in this phenomenon.

According to experiments carried out by the inventors named in the subject application, in the case of irradiating light onto organic-inorganic hybrid materials, there are other reactions involved in the above-mentioned phenomenon that can be found in hybrid materials but not in organic polymers. These other reactions are not simply other versions of photolocking itself, but rather are completely different reactions induced by photo-irradiation from photolocking. These other reactions cannot be reasonably expected when irradiating light onto pure organic polymers such as shown in *Chandross et al.*

Support for the foregoing facts can be found in literature references 1-4 attached hereto. The attached literature references 1-4 deal with subjects concerning the variation of refractive index caused by irradiation onto organic-inorganic hybrid materials, and confirm that the refractive index can be highly increased by light irradiation onto hybrid materials. This result cannot be explained solely by photolocking as disclosed in the *Chandross et al.* reference. Accordingly, for the foregoing reasons, as well as the reasons set forth in the Amendment dated December 29, 2004, claims 1-3 and 5-10 are patentable under 35 U.S.C. § 103(a) over the combination of *Kuramoto et al.* in view of *Chandross et al.*

Applicants respectfully request reconsideration of the rejection of claims 2-4 under 35 U.S.C. § 103(a) as being unpatentable over *Kuramoto et al.* in view of *Chandross et al.*, and further in view of U.S. Patent No. 6,144,795 to *Dawes et al.* Each of claims 2-4 ultimately depends from independent claim 1. The comments regarding the *Chandross et al.* reference set forth above in connection with the above-discussed obviousness rejection of claims 1-3 and 5-10 also apply to this rejection of claims 2-4. Accordingly, for at least the same reasons set forth above, claims 2-4 are patentable under 35 U.S.C. § 103(a) over the combination of *Kuramoto et al.* in view of *Chandross et al.*, and further in view of *Dawes et al.*

Applicants respectfully request reconsideration of the rejection of claims 1-3 and 5-10 under 35 U.S.C. § 103(a) as being unpatentable over *Chandross et al.* in view of U.S. Patent Application Publication No. US 2003/0195321 A1 to *Zha*. As explained in the Amendment dated December 29, 2004, and for the additional reasons set forth below, the combination of *Chandross et al.* in view of *Zha* does not raise a *prima facie* case of obviousness against the subject matter defined in claims 1-3 and 5-10.

The comments regarding the *Chandross et al.* reference set forth above in connection with the obviousness rejection of claims 1-3 and 5-10 based on the combination of *Kuramoto et al.* in view of *Chandross et al.* also apply to this obviousness rejection based on the combination of *Chandross et al.* in view of *Zha*. Thus, for at least the same reasons set forth above, the combination of the *Chandross et al.* reference and the *Zha* reference is improper and, therefore, does not raise a *prima facie* case of obviousness against the subject matter defined in claims 1-3 and 5-10.

Applicants respectfully request reconsideration of the rejection of claims 2-4 under 35 U.S.C. § 103(a) as being unpatentable over *Chandross et al.* in view of *Zha*, and further in *Dawes et al.* Each of claims 2-4 ultimately depends from independent claim 1. The comments regarding the *Chandross et al.* reference set forth above in connection with the obviousness rejection of claims 1-3 and 5-10 based on the combination of *Kuramoto et al.* in view of *Chandross et al.* also apply to this rejection of claims 2-4. Accordingly, for at least the same reasons set forth above, claims 2-4 are patentable under 35 U.S.C. § 103(a) over the combination of *Chandross et al.* in view of *Zha*, and further in view of *Dawes et al.*

In view of the foregoing, Applicants respectfully request reconsideration and reexamination of claims 1-10, and submit that these claims are in condition for allowance. Accordingly, a notice of allowance is respectfully requested. In the event a telephone

conversation would expedite the prosecution of this application, the Examiner may reach the undersigned at (408) 749-6902. If any additional fees are due in connection with the filing of this paper, then the Commissioner is authorized to charge such fees to Deposit Account No. 50-0805 (Order No. ASIAP119).

Respectfully submitted,
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Attachments:

- 1) "Direct Photo-Imprinting in High Photosensitive Organically Modified Germanosilicate (ORMOGSIL) Glasses" by Jae Hyeok Jang, Dong Jun Kang, and Byeong-Soo Bae;
- 2) "Direct photo-fabrication of multimode optical waveguide with an efficient refractive index modulation using photosensitive sol-gel hybrid materials" by Dong Jun Kang, Woo-Soo Kim, and Byeong-Soo Bae;
- 3) "Large Photoinduced Densification in Organically Modified Gemanosilicate Glasses" by Jae Hyeok Jang, Dong Jun Kang, and Byeong-Soo Bae; and
- 4) "Wavelength Dependent Photosensitivity in a Germanium-Doped Sol-Gel Hybrid Material for Direct Photo-patterning" by Jin-Ji Kim, Dong Jun Kang, and Byeong-Soo Bae.



Direct Photo-Imprinting in High Photosensitive Organically Modified Germanosilicate (ORMOGSIL) Glasses

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ABSTRACT

Direct photo-imprinting of both surface relief pattern and refractive index modulation upon the organically modified germanosilicate (ORMOGSIL) glass using its large volume change was performed by ultraviolet exposure. A large refractive index increase up to 10^{-2} is induced by ultraviolet-induced densification in the ORMOGSIL glasses. The photosensitivity in the ORMOGSIL glass was enhanced by introducing a photo-polymerizable methacrylate group in the glass structure. Also, a surface AFM scans and optical microscope images of unetched sample show that the volume compaction in the ultraviolet illuminated region is associated with periodic pattern inscription.

INTRODUCTION

Light-induced surface relief gratings have attracted attention because of their potential application for optical data storage, integrated optics or LC devices fabrication. Surface relief gratings are typically fabricated by mechanical, chemical, optical processing, and their combinations [1,2]. Since these processes are rather complex to reveal the precise surface structure, intensive research on the direct formation of surface relief gratings have been carried out in many research groups and companies all around the world in recent years [3-6]. Germanium doped silica glasses have received much attention because of the ultraviolet-induced refractive index change [7]. In this case, refractive index changes through defect reaction within the glass, but surface relief grating is rarely found [8-10]. However, recent our research on organically modified germanosilicate (ORMOGSIL) glasses fabricated by sol-gel method shows that the large refractive index change in ORMOGSIL glasses is predominantly due to the glass density increase induced by ultraviolet exposure rather than a defect chemistry [11].

In the present study, we report on the direct photo-inscription of both surface relief pattern

and refractive index modulation upon the organically modified germanosilicate (ORMOGSIL) glass using its large volume change induced by ultraviolet exposure. The shorter photo-imprinting time and the higher photosensitivity can be obtained by introducing photo-polymerizable organic units such as methacrylates into ORMOGSIL glass structure.

EXPERIMENTAL DETAILS

Organically modified germanosilicate glasses with Ge contents of 10, 15 and 20 mol% were prepared by the sol-gel method. Germanium Isopropoxide (GI, Aldrich) of 97%, Diethoxydimethylsilane (DMDES, Aldrich) of 97% and 3-(Trimethoxysilyl)propylmethacrylate (MPTMS, Aldrich) of 98% purity were used as the starting material. Since hydrolysis reaction of germanium isopropoxide was very fast compared with those of DMDES and MPTMS, DMDES and MPTMS were each prehydrolyzed and then germanium isopropoxide was added to the solutions. 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (Irgacure369, Aldrich) was used as photoinitiator in MPTMS/GI system. This photoinitiator undergoes a photo-cleavage to yield benzoyl radicals which initiate the photo-polymerization in the ORMOGSIL glass. The ORMOGSIL(I) and ORMOGSIL(II) glasses denote the DMDES/GI (unreactable organic) and MPTMS/GI (photo-polymerizable organic) system, respectively.

The ORMOGSIL glasses were illuminated by UV lamp (1KW Hg/Xe lamp, 220~260nm, Oriel 82521), which gave a power density of 45 mJ/cm². The refractive index of the glasses was measured at 632.8nm with a prism coupler (Metricon 2010). The density was measured by the Archimedes method using a Sartorius LA120S balance. Patterning of ORMOGSIL glass was carried out by ultraviolet fluence at 2500 J/cm² through a quartz contact mask. The surface morphology of the samples was observed with an Atomic Force Microscope (AFM, Park Scientific Instruments, Autoprobe 5M) and optical microscope.

RESULTS AND DISCUSSION

Figure 1 shows the refractive index change of the ORMOGSIL(I) glasses as a function of UV illumination. For all compositions of ORMOGSIL(I) glass, the refractive index increased linearly with UV fluence up to 2500 J/cm² and then approached a saturated level. The refractive index change of the 10 mol% Ge-doped ORMOGSIL(I) glass was about 10⁻². This is comparable with that seen with cold high pressure hydrogen soaking, which has led to germanium-doped fibers with the highest observed photosensitivity. Contrary to our expectation, for the

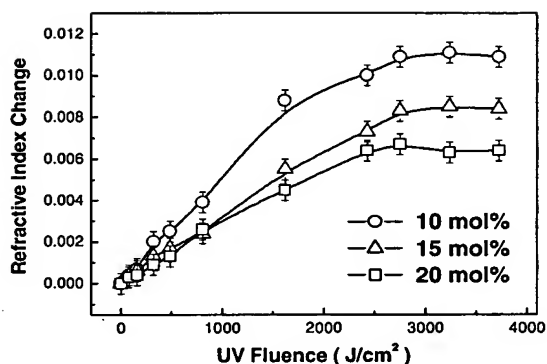


Figure 1. Changes in refractive index of 10, 15 and 20 mol% Ge-doped ORMOSIL(I) glasses with UV fluence of a 1000W Hg/Xe lamp

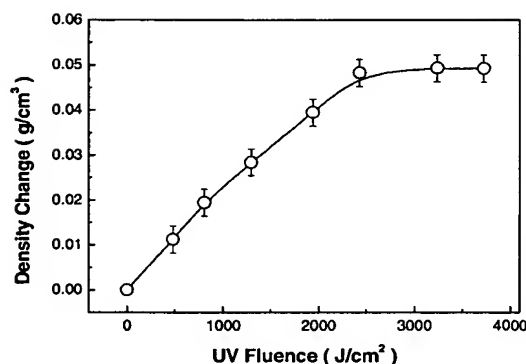


Figure 2. Density change in 20 mol% Ge-doped ORMOSIL(I) glass with UV fluence of a 1000W Hg/Xe lamp.

ORMOSIL(I) system, the refractive index change of 10 mol% Ge-doped ORMOSIL glass was larger than that of 20 mol% Ge-doped ORMOSIL glass. This result shows that the color-center model is not sufficient to explain large refractive index change in ORMOSIL(I) glass. Figure 2 shows the density change of 20 mol% Ge-doped ORMOSIL(I) glass with UV fluence. Density increases linearly with the UV fluence, the same behavior as observed in the refractive index change behavior. In addition, we have found recently that the refractive index change in ORMOSIL(I) glass is mainly due to the structural densification by reduction of the average intertetrahedral bonding angle θ from the shifts in frequency of the Raman bands with the UV illumination [11].

Certain monomers, notably styrene and methyl methacrylate and some strained-ring cycloalkenes, undergo photoinduced chain polymerization. This polymerization also induces refractive index increase [12]. Thus, we fabricated the organic-inorganic hybrid silica glasses having higher photosensitivity by introduction of methacrylates instead of methyl groups. Figure 3 shows the refractive index change and thickness of ORMOSIL(II) glass as a function of UV illumination. The ORMOSIL(II) glass reacts more quickly to the UV light and produces higher saturated index changes rather than that in figure 1. And the gradual decrease in glass thickness with UV exposure indicates that the refractive index change in ORMOSIL glass is associated with volume compaction induced by UV exposure.

The ORMOSIL glasses are direct photopatternable without any developing steps such as wet etching. Figure 4 shows AFM and optical microscope image of direct photo-imprinted

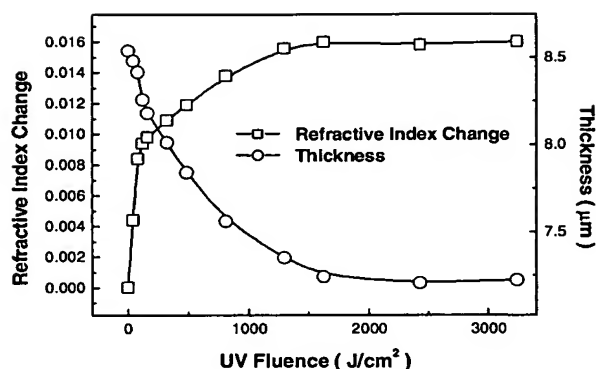


Figure 3. Refractive index change in 10 mol% Ge-doped ORMOSIL(II) glass with UV fluence of a 1000W Hg/Xe lamp.

pattern written in the ORMOSIL(I) glasses. The three-dimensional view of AFM revealed that a periodic pattern of a sinusoid wave with a 6 μm period spacing and 65 nm changes in depth from the original surface was formed upon the ORMOSIL(I) glass. A photoinduced direct densification occurs in the UV illuminated regions. This regular surface modulation has attracted attention for optical device applications such as diffractive optical elements, optical switching, optical recording, channel waveguides, microlens and antireflection coatings, etc. Figure 5 shows

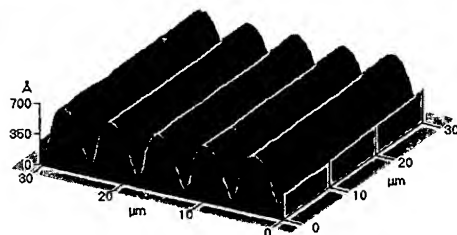
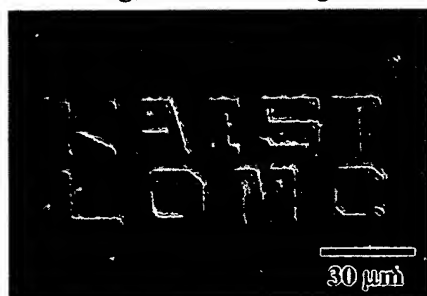


Figure 4. Optical microscope and AFM image of illustrated and line pattern written in the ORMOSIL(I) glass, respectively.

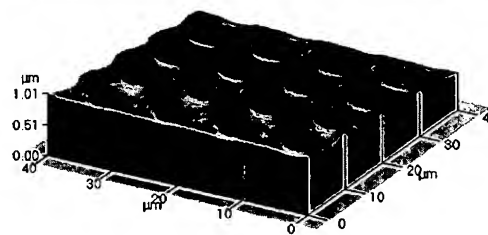
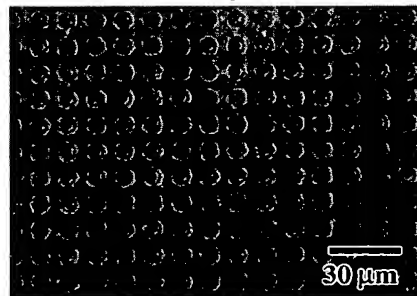


Figure 5. Optical microscope and AFM image of an array of microlenses written in the ORMOSIL(II) glass, respectively.

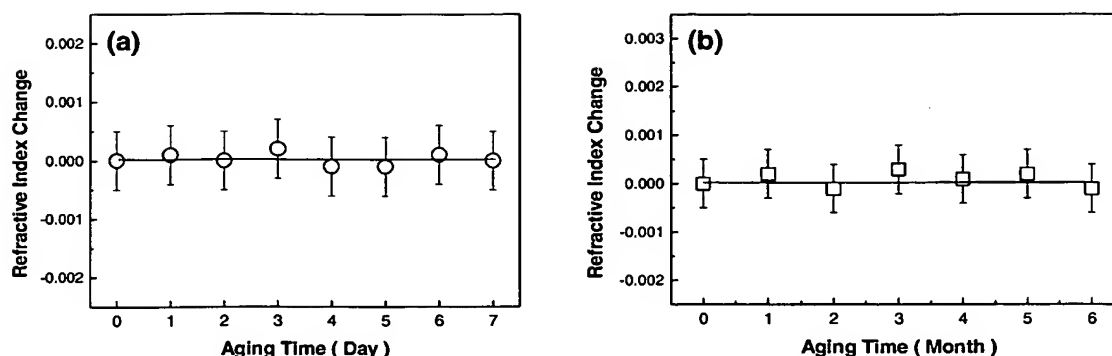


Figure 6. Change in refractive index of the 10 mol% Ge-doped ORMOSIL glasses with the aging time at (a) 100 °C and (b) room temperature.

an array of microlenses, each with a diameter of 5 μm , inscribed on the ORMOSIL(II) glass. The depth change from the original surface is about 400 nm, which is larger than that in the ORMOSIL(I) glass. This result also indicates that the direct photo-patterning in the ORMOSIL(II) glass is more efficient rather than that in the ORMOSIL(I) glass.

To examine the thermal stability of the ORMOSIL glass, we measured the refractive index of UV-exposed ORMOSIL glass with aging time at 100 °C and room temperature. As shown in figure 6, no changes in refractive index of the ORMOSIL glasses with UV exposure were detected. This result indicated that the photosensitivity in the ORMOSIL glass is thermally stable up to 100 °C and also permanent at room temperature.

No doubt refractive index modulations based on GeO_2 doped silica glasses have many attractive and unique features. Nevertheless they have also their limits. Most apparent limitation seems to be their limited wavelength tenability and stress responsivity. This could be a fundamental limit that restricts silica glasses from being used in some of the important applications. Wavelength tenability will be a crucial feature required for future broadcasting and reconfigurable dense wavelength division multiplexer(DWDM) systems. The main reason for the poor tenability is clearly linked to the high rigidity of silica glass. Likewise the poor stress responsivity is related to its relatively large Young's modulus. Therefore, the high photosensitive ORMOSIL glass is attractive for its good flexibility, low cost and ease of handling.

CONCLUSIONS

This study reports a direct photoinduced inscription of both surface relief pattern and

refractive index modulation upon the organically modified germanosilicate (ORMOGSIL) glass fabricated by sol-gel method. The refractive index modulation in ORMOGSIL glass with UV exposure is accompanied with large volume change induced by the structural densification. The shorter photo-imprinting time and the higher photosensitivity can be obtained by introducing polymerizable organic units such as methacrylates into ORMOGSIL glass. In addition, photosensitivity in ORMOGSIL glass is thermally stable.

ACKNOWLEDGEMENTS

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Direct photo-fabrication of multimode optical waveguide with an efficient refractive index modulation using photosensitive sol-gel hybrid materials

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Photosensitive sol-gel hybrid materials (Hybrimers) exhibited a thick film property, an efficient refractive index tunability through the control of compositions and a high photosensitivity on UV exposure. The materials were used for the direct photo-fabrication of the multimode optical waveguide (MOW) with a large core structure. Due to the outstanding optical properties of these materials, problems and complexities associated with the fabrication of multimode optical waveguide (MOW) could be overcome and the multimode optical waveguide (MOW) with good propagation performance could be easily fabricated. Importantly, a low propagation loss as low as 0.13 dB cm^{-1} at 850 nm could be obtained.

Keywords

photosensitive sol-gel hybrid material, photosensitivity, direct photo-fabrication, multimode optical waveguide

An optical waveguide (OW) device is an important component for use in optical interconnection, optical signal processing and optical connection in optical communication systems.¹⁻⁵ Currently, rapidly increasing demand for communication causes a rapid increase in the use of an OW device and the ability to easily arrange optical fibers is particularly needed in order rapidly and efficiently to transfer an optical signal. To satisfy the above requirement, the fabrication of a multimode optical waveguide (MOW) device having a large core structure is considered very important, and, recently, has been actively studied.⁶⁻¹⁰ In general, the OW device is produced using a semiconductor production technology including lithographic or etching techniques and the clad layer or the core layer is typically formed through a spin coating process and a deposition process, and is made of silica or polymers having different refractive indices. However, these methods are rather complex and need several steps, which increases the cost of the OW device and reduces reliability. Moreover, silica exhibits the limitations in obtaining the large refractive index change between the core and clad layers and in fabricating the large core structure and polymeric OW has the low thermal stability due to the low thermal stability of polymer materials. Accordingly, the use of the silica and polymer materials is problematic in that it is difficult to produce a MOW for optical communication with a high performance. For these reasons, many studies have concentrated on simplifying the fabrication process as well as studying the optimum materials for a MOW.

In recent years, the sol-gel hybrid materials (Hybrimers) were found to produce a thick film over 10 microns or more by single spin-coating, which is a crucial factor for a MOW with a large core structure and could reduce the steps in the fabrication of a MOW. Moreover, these hybrimers exhibited the high photosensitivity, meaning

the larger refractive index and volume changes on UV exposure. The photosensitivity of these materials could be increased by the simple addition of photoactive molecules, which would derive the high performance of a MOW. Also, these materials have the potential to be used in simple single-step photo-patterning due to the simultaneous changes in both refractive index and volume without any etching step.¹¹⁻¹³ Thus, these photosensitive hybrimers have been widely used for the photo-fabrication of highly efficient optical devices.^{14, 15} Therefore, the photosensitive hybrimers are good candidates for producing a high efficiency MOW which includes a large core structure having a size of 10 microns or more.

In this study, we thus sought to fabricate a high-efficiency MOW with crack-free large core structures on a clad layer using photosensitive hybrimers with outstanding optical properties through a photo mask. Finally, we simply manufactured a MOW with the efficient refractive index modulation between the core and the clad layer and a low propagation loss by the direct photo-fabrication.

In our experiments, the hybrimers were prepared using methacryloxypropyl-trimethoxysilane (MPTMS, Aldrich), perfluoroalkylsilane (PFAS, Toshiba), diphenylsilanediol (DPSD, TCI) as precursors, and barium hydroxide monohydrate ($\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$, Aldrich) as a catalyst to promote the poly-condensation reaction among these precursors. The DPSD content was fixed at 50 mol% and the content ratio of PFAS with the role of decreasing the refractive index due to perfluoroalkyl group of PFAS was changed from 10 % to 12.5 % for the efficient refractive index difference of the core and clad layer, maintaining 50 mol % in the total proportion of MPTMS and PFAS, and barium hydroxide monohydrate (about 0.1 mol% of the precursors) was added as a catalyst, as described in previous reports for fabricating a MOW.¹⁶ The obtained hybrimers were mixed with a photoinitiator,

benzylidimethylketal (BDK, Aldrich), which facilitates various photoinduced reactions as well as increases the photosensitivity by UV light exposure. In particular, the different contents of BDK were added in the respective hybrimers for UV curing of a clad layer and the photo-fabrication of a large core structure with a considerable refractive index modulation in a core layer. The photosensitive hybrimers containing BDK were filtered using a 0.45 μm size filter to remove the remaining $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ and dust. These photosensitive hybrimers were used for the direct photo-fabrication of a MOW.

The direct photo-fabrication process of a MOW is schematically illustrated in Fig. 1, which shows a typical experiment, to fabricate a MOW. First, photosensitive hybrimers with PFAS content ratio of 12.5 % and BDK of 2 wt% are spin-coated on p-type Si (100) wafers for the formation of under clad layer with 1000 rpm spinning speed for 30 seconds. After that, UV curing was carried out for 30s with a Hg UV lamp ($\lambda=350 \sim 390 \text{ nm}$, optical power density= 100mWcm^{-2}) and then consolidated by baking at 150°C for 4 hours. Second, photosensitive hybrimers with PFAS content ratio of 10 % and BDK of 10 wt% are spin-coated on clad layer for the formation of core layer with 500 rpm spinning speed for 30 seconds. After that, direct photo-fabrication of large core structure in core layer was carried out for 30 min with a Hg UV lamp using a photo mask and then heat treatment of patterned MOW was accomplished at 150°C for 4 hours for the efficient refractive index difference between large core structure and around core areas including clad layer. Finally, for the passivation of photo-fabricated MOW, photosensitive hybrimers with the same composition as under clad layer are spin-coated on core layer with 1000 rpm spinning speed for 30 seconds. After that, UV curing was carried out for 30s with a Hg UV

lamp and then consolidated by baking at 150°C for 4 hours for a chemically and mechanically stable MOW.

Figure 2 shows an optical micrograph (a) and scanning electron micrograph (b) of a MOW including core structure and under clad layer directly photo-fabricated using a photo mask. As shown in Fig. 2, a thick film close to 40 μm for core layer with a large core structure could be formed evenly on under clad layer with 15 μm thickness by single spin-coating and no cracks appear after UV and thermal curing by using the photosensitive hybrimers. Also, The MOW exhibited the good shaped large core structure with 40 μm width by the negative-type sensitivity of photosensitive hybrimers on UV exposure, which related to the photoreactions between the hybrimer matrix and BDK within the exposed core. These series of photoinduced reactions would be related to various reactions such as photopolymerization due to photodecomposition of BDK, photolocking such as the reaction between BDK radicals and the attachment of BDK radicals to the matrix, and photomigration due to the concentration gradient of BDK between unexposed areas and exposed core.^{11-15, 17} Thus, the photosensitive hybrimers with a thick film property and a good photo-patternability can be potential materials for the direct photo-fabrication of a MOW. These series of photoinduced reactions in photosensitive hybrimers would also cause the considerable refractive index increase in large core structure of a MOW as well as the volume change. BDK in the exposed core was fixed within the hybrimer matrix by various photoinduced reactions and then not removed by heating and drying. On the other hand, BDK in the unexposed area were volatile and easily removed by baking. After baking, the different characteristics of BDK between the UV exposed core area and unexposed around core areas in a MOW would make the large refractive index changes. In addition, the photoinduced reactions in inorganic part of

the photosensitive hybrimers such as photoinduced condensation and densification would be occurred within the UV exposed core area in a MOW, which also partially makes a role in increasing the refractive index. As shown in Fig 2 (b), the different contrast due to the refractive index difference between UV exposed core structure and unexposed around core areas including under clad layer could be detected, which supports the refractive index increase in core structure by various photoinduced reactions of photosensitive hybrimers on UV exposure. The respective refractive index of clad layer and core layer in a photo-fabricated MOW was 1.486 and 1.501 at 1550 nm and the refractive index of a photo-fabricated core structure would be much higher than other areas in a fabricated MOW due to the strong photoinduced reactions within core structure by UV exposure through a photo mask.

In order to confirm the refractive index modulation between UV exposed core structure and unexposed around core areas in a MOW, the effect of refractive index increase in the core structure by the photoinduced reactions in photosensitive hybrimers was measured in a reflection mode by using Near-Field Optical Scanning Microscope (NSOM) with an AR laser ($\lambda=488$ nm) as probing source. Figure 3 shows 3 D NSOM image (a) and 2D NSOM line profile of optical intensity of reflection representing the refractive index difference between core and around core areas of a MOW (b). Optical intensity profile representing refractive index difference between core and around core areas was remarkably different and optical intensity of core structure in a MOW is much higher than that of around core areas, as shown in Fig 3. UV exposed core structure has a higher refractive index than unexposed around core areas, which related directly to the various photoinduced reactions between hybrimer matrix and BDK within UV exposed core through a photo mask. The direct photo-

fabricated MOW exhibiting strong refractive index difference between large core structure and around core areas is thus very good candidate of a high-efficiency MOW.

In order to evaluate the propagation performance from the directly photo-fabricated MOW, the light propagation property and propagation loss were checked. Figure 4(a) exhibits the light propagation near-field image and Figure 4(b) shows the propagation loss of the directly photo-fabricated MOW. Our directly photo-fabricated MOW showed a strong light propagation performance and the propagation loss measured by cut back method was as low as approximately 0.13 dB cm^{-1} at 850 nm wavelength. These good light propagation performance and low propagation loss are due to the low optical absorption of hybrimers in addition to the efficient refractive index difference between core structure and around core areas by high photosensitivity due to various photoinduced reactions of photosensitive hybrimers. Optical absorption is one of the dominant factors considered in the propagation loss of an OW. The hybrimers exhibited low optical absorption because it contains little amount of silanol group. Moreover, in these hybrimers contains perfluoralkyl group, which partially lead to substitute carbon-hydrogen to carbon-fluorine. This reduces the absorption over the whole detected spectral range. Therefore, the MOW directly photo-fabricated using the photosensitive hybrimers with the outstanding optical properties can have the high efficiency such as a rapid and efficient transfer of optical signal due to the large core structure and low propagation loss and is suitable for various optical applications, including optical signal processing and optical connection in optical communication systems.

In conclusion, the photosensitive hybrimers which can form thick film exhibited an efficient refractive index tunability and a high photosensitivity. The MOW with a large core structure can be directly fabricated on the photo-masked thick

photosensitive hybrimer film by simple UV exposure. The photo-fabricated MOW exhibited the efficient refractive index modulation between large core structure and clad area. Finally, the photo-fabricated MOW showed good propagation performance and a propagation loss as low as 0.13 dB cm^{-1} at 850 nm.

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Captions

FIG. 1. Schematic diagram of direct photo-fabrication of a MOW using photosensitive hybrimers. (a) Formation of under clad layer through UV and thermal curing, (b) spin coating of core layer on under clad layer, (c) direct photo-fabrication of large core structure in core layer with a photo mask, (d) Final formation of over clad layer through UV and thermal curing.

FIG. 2. Optical micrograph (a) and scanning electron micrograph (b) of a MOW including large core structure and under clad layer directly photo-fabricated using a photo mask.

FIG. 3. 3D NSOM image (a) and 2D NSOM line profile of optical intensity representing the refractive index profile of core area of a MOW (b).

FIG. 4. Light propagation near-field image (a) and propagation loss of the directly photo-fabricated MOW (b).

photo mask

Fig. 1.

Dong Jun Kang

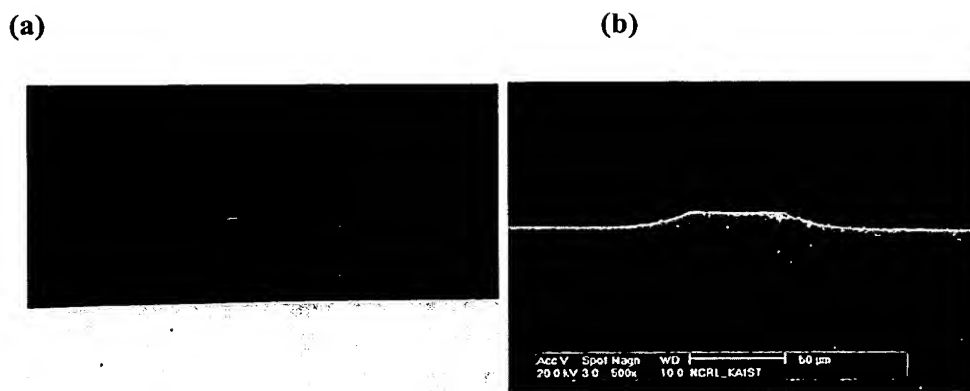


Fig. 2.

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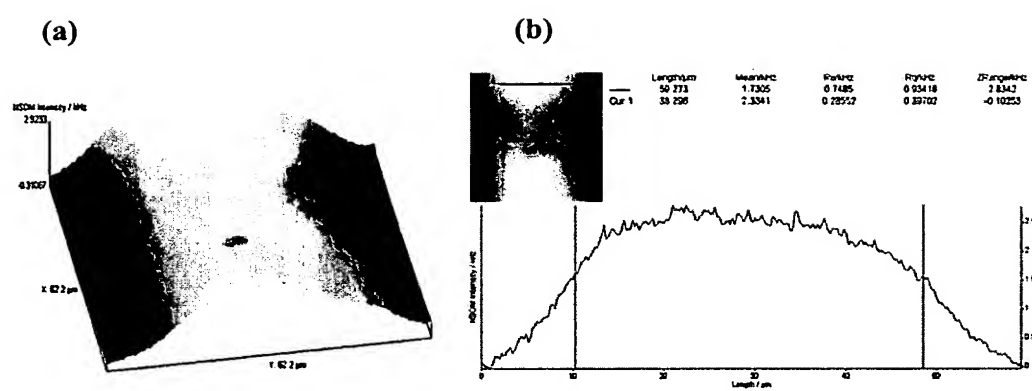
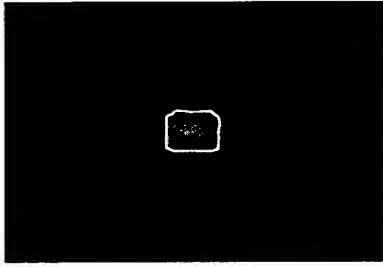


Fig. 3.

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(a)



(b)

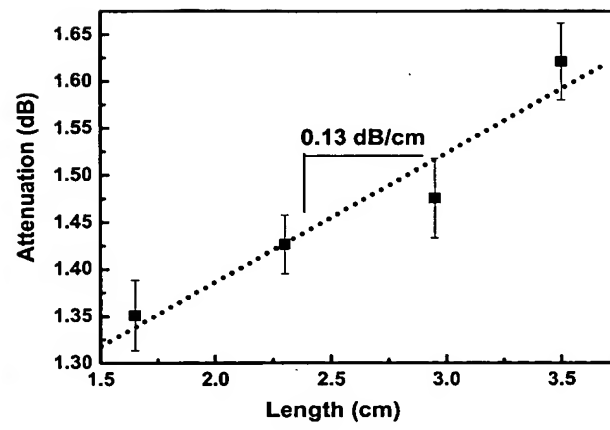


Fig. 4.

Dong Jun Kang

Large Photoinduced Densification in Organically Modified Germanosilicate Glasses

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Organically modified germanosilicate (ORMOGSIL) glasses prepared by a sol–gel method showed a large refractive index change on ultraviolet exposure. The large photoinduced refractive index change in the ORMOGSIL glasses is mainly due to the structural densification caused by ultraviolet irradiation. The shifts in frequency of the Raman bands measured at room temperature reveal structural densification by reduction of the average intertetrahedral bonding angle θ in the ORMOGSIL glasses. Surface relief patterns by photoinduced densification were directly inscribed on the ORMOGSIL glasses.

I. Introduction

PHOTOSENSITIVE effect is a permanent change in the refractive index of a medium by exposure to light. The refractive index modulation in photograph polymers^{1,2} and photonic crystals^{3,4} can be accompanied with the surface relief modulation, induced by molecular structural changes. This regular surface modulation has attracted attention for optical device applications such as diffractive optical elements, optical switching devices, optical information storage, channel waveguides, and antireflection coatings, etc. Photosensitivity in germanium-doped silica glass has been investigated for grating-based devices with high reflectivities and broad bandwidths that have numerous applications in telecommunications and sensor networks.⁵ In this case, the refractive index changes through a defect reaction within the glass,^{6,7} but a surface relief pattern is rarely found. Some of the recent researches have been focused on making these glasses react more quickly to ultraviolet light and produce higher saturated index changes. In recent years, organically modified silica glasses have begun to receive attention because they can combine the properties of both inorganic and organic compounds, which promise numerous optical applications.^{8,9}

In the present work, we investigated the photosensitivity of organically modified germanosilicate (ORMOGSIL) glasses fabricated by the sol–gel method. We examined the effect of the organic modifier in the enhanced photosensitivity and directly inscribed the surface relief modulation on the ORMOGSIL glass by ultraviolet exposure through a quartz contact mask.

II. Experimental Procedure

Germanium isopropoxide ($\text{Ge}(\text{OC}_3\text{H}_7)_4$, GI) and diethoxydimethylsilane ($(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$, DMEDES) were used as the starting precursors. The molar ratio of GI to DMEDES was 1:4. Since the hydrolysis reaction of GI was very fast compared with that of DMEDES, DMEDES was prehydrolyzed with hydrochloric acid as a catalyst for 2 h, and then GI diluted with isopropyl alcohol (1:2 molar ratio) was added to the solution. After being stirred for 24 h, the prepared sol solutions were gelled in a closed Petri dish at 50°C in air for 1 week, during which the inorganic precursor hydrolyzes and condenses into a gel–glass transition network. After sintering at 250°C for 8 h under reduced ($\text{H}_2/\text{N}_2 = 1:9$ volume ratio) atmosphere, we obtained optically transparent ORMOGSIL glasses. Two methyl groups in DMEDES can act as a modifier in the ORMOGSIL glass network, as can be seen in Fig. 1.

Ultraviolet (220–260 nm) light irradiation was performed with a 1000-W Hg/Xg lamp (82511, Oriel, Stratford, CT), which gives a power density of 45 mJ/cm². Refractive index was measured using a prism coupler (Model 2010, Metricon, Pennington, NJ) at 632.8 nm. The density of the ORMOGSIL glass was measured by the Archimedes method using a balance (LA120S, Sartorius, Goettingen, Germany). Raman spectra were measured with a 488-nm Ar–Kr ion laser (Coherent Innova 70 Series, Laser Innovations, Moorpark, CA) and double grating monochromator

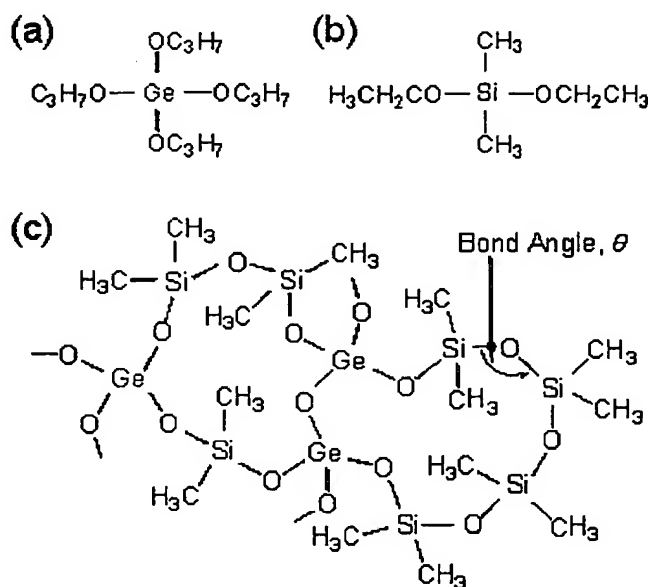


Fig. 1. Chemical structure of the sol–gel precursors and the ORMOGSIL glass: (a) germanium isopropoxide; (b) diethoxydimethylsilane; (c) ORMOGSIL glass. Methyl groups act as modifier in the silica glass network.

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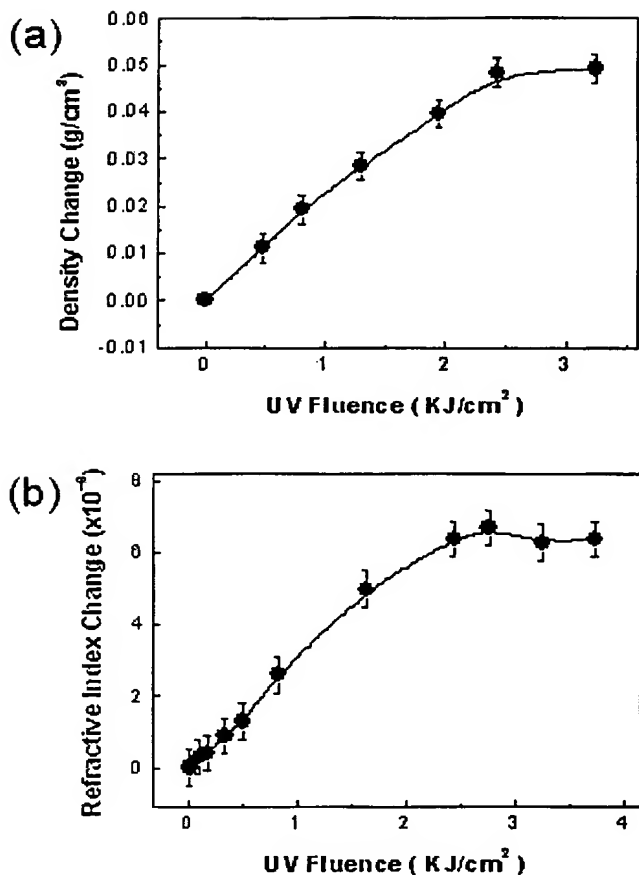


Fig. 2. Change in (a) refractive index and (b) density of the ORMOSIL glasses with the ultraviolet fluence of the 1000-W Hg/Xe lamp (220–260 nm, 45 mJ/cm²).

(U-1000, Jobin Yvon, Inc., Edison, NJ). The surface topology of the ORMOSIL glass was observed by atomic force microscopy (AFM; Autoprobe 5M, Park Scientific Instruments, Woodbury, NY) in a cyclic contact mode.

III. Results and Discussion

Figure 2 shows the refractive index change and the density change of the ORMOSIL glasses with the ultraviolet (UV) fluence. Refractive index increases linearly with the UV fluence up to 2500 J/cm² and then saturates at 6.5×10^{-3} . The density increases linearly up to 0.05 g/cm³ with the UV fluence, the same behavior as that seen for the refractive index change shown in Fig. 2(a). A refractive index change Δn is given by the differential form of the Lorentz–Lorenz equation:¹⁰

$$\Delta n = \frac{(n^2 - 1)(n^2 + 2)}{6n^2} \left(\frac{\Delta \alpha}{\alpha} - \frac{\Delta V}{V} \right) \quad (1)$$

Assuming that a change in polarizability of the ORMOSIL glass is zero with UV irradiation, a refractive index change can be written as follows:

$$\Delta n = \frac{(n^2 - 1)(n^2 + 2)}{6n^2} \left(\frac{\Delta \rho}{\rho} \right) \quad (2)$$

The calculated refractive index change from the Lorentz–Lorenz equation is about 8×10^{-3} , which is in agreement with the experimental data.

Zachariasen's random network theory¹¹ provides the basic rules for the modeling of silica glass structures. The simple description of the silica glass structure is based on rings, which are closed circuits along nodal connections, for example through tetrahedra in the tetrahedral network. Angle θ between two neighboring tetrahedra (the Si–O–Si angle) is called the bond angle, as shown in Fig. 1. The densification of the glass structure is ascribed mostly to the variations in θ . Raman scattering spectroscopy was used to ascertain the structural changes of the ORMOSIL glasses with UV irradiation. The frequency shifts in the Raman bands reveal structural changes in the glass. The results are shown in Fig. 3. The

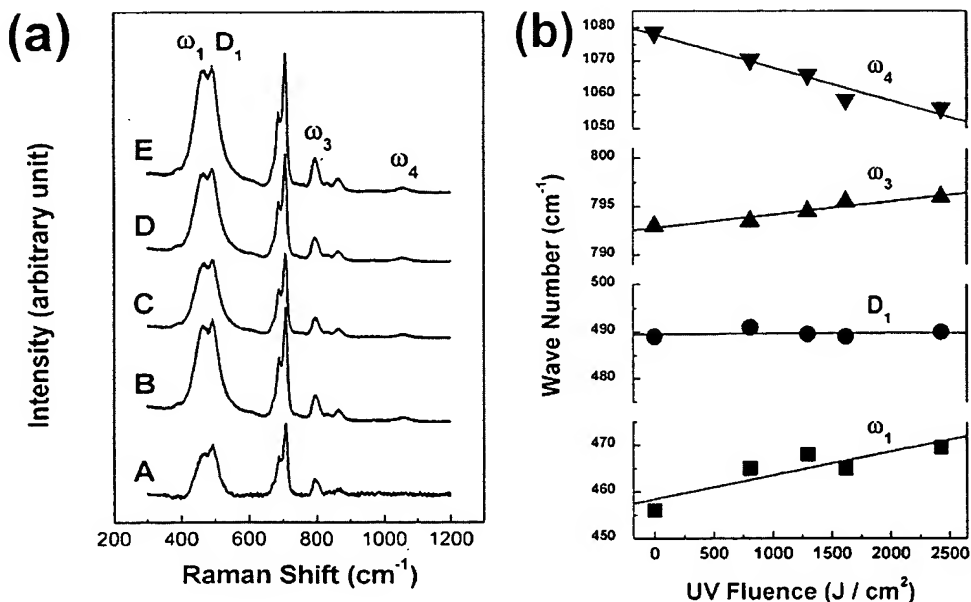


Fig. 3. (a) Stoke-scattered Raman spectra observed in ORMOSIL glasses with the ultraviolet fluence. Traces A–E are 0, 800, 1300, 1600, and 2500 J/cm², respectively. (b) Plot of the peak positions of the Raman features as a function of ultraviolet fluence. Lines drawn through the points are least-squares fits to the data.

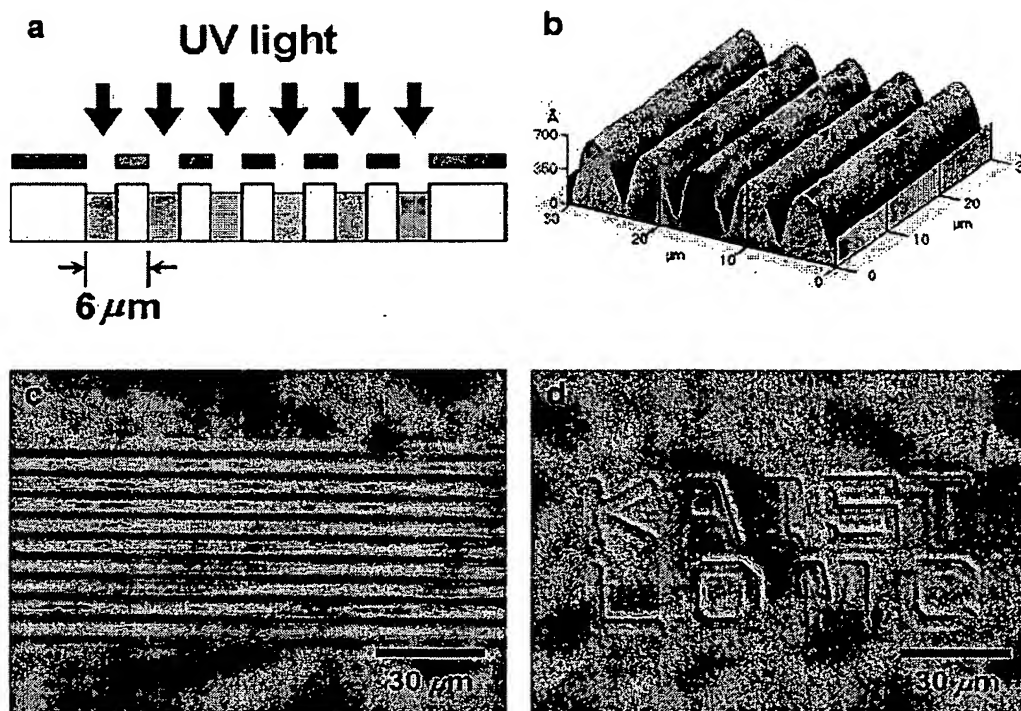


Fig. 4. (a) Schematic representation of ultraviolet direct patterning. Volume compaction occurs in the UV-illuminated regions. (b) AFM and (c, d) optical microscope images of direct photopatterning on the ORMOSIL glass.

460- and 490-cm⁻¹ bands have been assigned to the presence of six-membered rings and four-membered rings of SiO₄ tetrahedra, which are attributed to the Si–O–Si symmetric stretching vibration.^{12,13} The 700-cm⁻¹ band attributed to the methyl group acting as the organic modifier in the glass network is not affected by the UV irradiation. Figure 3(b) shows the change in frequencies of the Raman bands as a function of UV fluence. The ω_1 and ω_3 bands have shifted to the higher frequency side, while the ω_4 band has shifted to the lower frequency side upon UV illumination. However, the D_1 frequency has been found to be independent of UV fluence.

It is well-known that ω_i frequencies are related to the Si–O–Si bridging bond angle θ by a central-force idealized-continuous-random-network (CF-ICRN) theory.¹⁴ Assuming that all force constants are zero except for the Si–O bond-stretching constant α , the relationship between the shift in Raman frequencies $\Delta\omega_i$ and the change in bond angle $\Delta\theta$ is expressed as follows:

$$\Delta\omega_i = \pm(\alpha/m_O)(\sin \theta)(\Delta\theta/2\omega_i) \quad (3)$$

Here, ω_i is the angular frequency (rad/s) of Si–O–Si stretching while m_O is the mass of the oxygen atom. The sign is negative for $i = 1$ and 3 and positive for $i = 4$. Therefore, as shown in Fig. 3, $\Delta\omega_i$ is positive for ω_1 and ω_3 and negative for ω_4 and the intertetrahedral θ decreases from Eq. (3), indicating that the structural densification occurs in the ORMOSIL glass with UV irradiation. A molecular-dynamics simulation of Rino *et al.*¹⁵ indicates that SiO₄ tetrahedra organize in n -fold rings with $3 \leq n \leq 10$, $n = 6$ being the most frequent value in both amorphous and molten silica. And, also, the GeO₂ glass is mainly composed of six-membered rings of GeO₄ tetrahedra connected in a random three-dimensional network because of the larger size of Ge atoms compared with Si atoms. It is well-known that the Ge–O bonds are weaker than Si–O bonds and they can be more readily broken by low-energy radiation. Moreover, it was found in this study that the organically modified silica glass without germanium oxide was not photosensitive. Thus, the behavior of the ω_1 band with UV exposure is due to the breakup and rearrangement of the Ge–O

bonds in the ORMOSIL glass network. In addition, the decrease in connectivity of the three-dimensional network caused by the organic modifier facilitates the structural rearrangement of the ORMOSIL glass. The calculated Si–O–Si $\Delta\theta$ from $\Delta\omega_1$, which is related to six-membered rings of silica tetrahedra, is about -1.64° using $\alpha = 535$ N/m and $\theta = 130^\circ$.¹³ Although there are no data on the relationship between $\Delta\theta$ and the density change $\Delta\rho$ or Δn for the ORMOSIL glasses, Δn of the ORMOSIL glass can be roughly estimated using the relationship for the silica glass. Devine¹⁶ reported that $\Delta\rho$ and $\Delta\theta$ result in the relationship for the silica glass:

$$\Delta\rho = 0.0367 \times \Delta\theta \quad (4)$$

From the calculated bonding angle change, we can roughly estimate Δn of the ORMOSIL glass by using relations (1) and (4). The estimated refractive index change is about 10^{-2} , which is in good agreement with the experimental data shown in Fig. 2(a). Therefore, Raman spectra confirm that the density change induced by a change in the bond structure of the silica network accounts for a major part of the photosensitivity in ORMOSIL glasses.

Surface relief patterning in the ORMOSIL glass was photo-fabricated by UV fluence of 2500 J/cm² through a quartz contact mask. Figure 4(b) represents an AFM image of the lined pattern inscribed on the surface of the glass, and Figs. 4(c) and (d) show $\times 400$ magnified views of the lined and illustrated patterns written on the ORMOSIL glass as imaged through the optical microscope. The three-dimensional view of AFM revealed that the volume compaction in the UV-illuminated region is associated with periodic pattern inscription. This is direct evidence for the photoinduced densification in the ORMOSIL glasses.

IV. Conclusions

We suggest that the large photoinduced refractive index change in the ORMOSIL glass is related to the structural densification caused by UV irradiation. The shifts in frequency of the Raman

bands reveal structural densification by reduction of the average intertetrahedral bonding angle θ in the ORMOSIL glass. Although the writing time for the periodic refractive index modulation is relatively slow, this large index change and the direct inscription of a relief pattern on the ORMOSIL glass have allowed easy development of grating-based devices that have a wide range of optical device applications.

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Wavelength Dependent Photosensitivity in a Germanium-Doped Sol-Gel Hybrid Material for Direct Photo-patterning **

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Abstract

Photosensitivity, as evidenced by permanent changes in refractive index and volume upon light exposure, is observed in a germanium-doped methacrylate hybrid material (hybrimer) and found to depend on the wavelength of the UV light. Exposure to short wavelength UV illumination (220–260nm) results in very high photosensitivity with changes in refractive index ($\Delta n \approx 0.0164$) and film thickness ($\Delta t \approx -40\%$) being mainly due to photo-polymerization and Ge-related densification. In contrast, the hybrimer is hardly photosensitive to light in the long UV wavelength range (350–390nm). Direct photo-patterning of a single circle on the hybrimer film creates a concave lens-like topography upon illumination with UV light of short wavelength and a convex lens-like one upon illumination with UV light of long wavelength.

Keywords: photo-patterning, hybrid material, photosensitivity, photo-polymerization, Ge-related densification

1. Introduction

Micro-optical structures have been studied widely due to their increased use in compact optoelectronics, optical computing and optical communication devices.

Conventional micro-fabrication is carried out with a multi-step process that includes an etching or developing stage.^[1,2] The process can be simplified by using photosensitive materials that can undergo permanent changes to their refractive index and volume simply by exposure to light. This would allow the fabrication of micro-optical structures without an etching or developing step. It has been known that Ge-doped silica glasses,^[3] photo-polymers,^[4] and azo-polymers^[5] are typical photosensitive materials which can have their refractive index modulated or surface relief micro-optical structures created in them just by exposure to UV light. However, these materials possess comparatively little photosensitivity, are sensitive to heat, and often not transparent enough to be used in the fabrication of micro-optical devices.

Recently, it has been reported that the sol-gel derived inorganic-organic hybrid materials (hybrimers) also exhibit high photosensitivity upon illumination with UV light and can be used in the fabrication of many micro-optical devices such as waveguides,^[6] micro-lenses,^[7] and gratings.^[8-9] In the photosensitive hybrimers, various photosensitivity mechanisms such as photo-polymerization,^[10,11] photo-locking,^[12-15] photo-migration,^[16] photo-decomposition,^[17,18] and photo-densification^[19,20] have been proposed to explain the different types of change in the refractive index and volume. It would seem that the photosensitivity of the hybrimer can be maximized by optimizing

both of the photosensitive mechanisms of the inorganic and organic components. In fact it has been found that Ge-doped methacrylate hybrimer consisting of methacrylate and Ge-doped silica in the molecular structure shows high photosensitivity in the form of a refractive index increase and accompanying volume compaction. Both of the Ge-related densification in the silica network and the photo-polymerization of methacrylate induced by illumination with UV light contribute to the photosensitivity. It is known that the photo-induced densification of Ge-doped silica glass occurs only for light in the deep UV region of the spectrum.^[21] Also, it has been reported that the photo-polymerization of acrylates is likewise dependent on the wavelength of the UV light employed.^[22] Thus, it is expected that the photosensitivity of the Ge-doped methacrylate hybrimer will be highly sensitive to the wavelength of the UV light employed as the photosensitivity mechanisms will vary depending on the wavelength of the illuminating light.

In this study, we first examined the photosensitivity mechanisms of the Ge-doped methacrylate hybrimer as a function of the wavelength of the illuminating light. Then, the change in the refractive index (Δn) and the film thickness (Δt) induced by irradiation two UV lamps yielding different wavelength light were investigated. It was found that the photosensitivity mechanism relied on the wavelength of the illuminating light. Finally,

we demonstrated the fabrication of lens-like shapes by photo-patterning of the hybrimer using the two different UV lamps.

2. Results and discussion

The Ge-doped methacrylate hybrimer films were irradiated by a Hg/Xe lamp and a Hg lamp which possess different UV spectral ranges of 220–260nm and 350–390nm, respectively. Fig.1 shows the change in the refractive index and the thickness of the films as a function of UV light fluence for both the UV lamps. Irradiating with the Hg/Xe

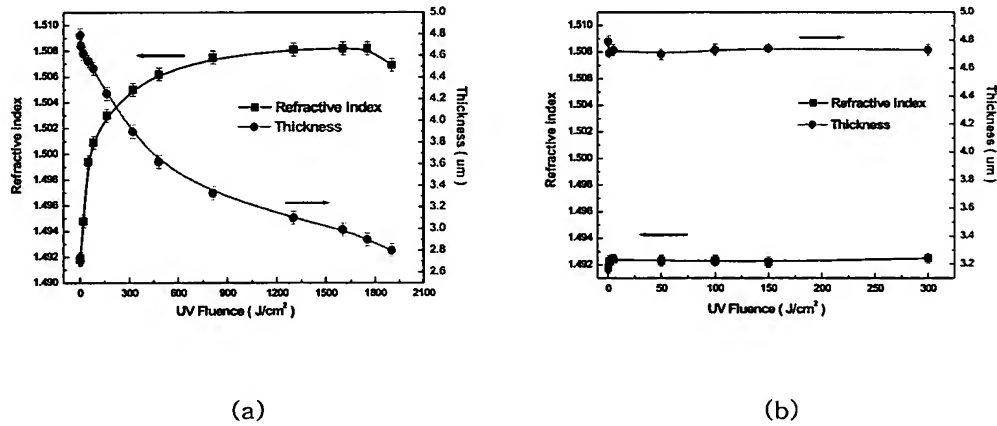


Figure 1. Change in refractive index and film thickness of the Ge-doped methacrylate hybrimer as a function of UV light fluence when illuminated by (a) a Hg/Xe lamp (220–260nm) and (b) a Hg lamp (350–390nm)

lamp caused an initial drastic change in the refractive index and the film thickness.

These effects were seen to saturate after exposure for long times. On the other hand, the Hg lamp illumination barely changed the refractive index and the film thickness with the initial increase being small.

To summarize, the Hg/Xe lamp results in high photosensitivity and the Hg lamp resulted in low photosensitivity. This implies that the photosensitivity of the Ge-doped methacrylate hybrimer depends heavily on the wavelength of the UV light. The different photosensitivity mechanisms of the Ge-doped methacrylate hybrimer were examined as a function of the wavelength of the irradiating light.

2.1 Photo-polymerization with a photo-initiator

Fig. 2(a) shows the evolution of the Fourier transform infrared (FR-IR) spectra of the Ge-doped methacrylate hybrimer as a function of fluence using the Hg/Xe lamp. Exposure to the short wavelength radiation of the Hg/Xe lamp reduces the intensity of the $\nu(\text{C}=\text{C})$ peak at 1638cm^{-1} and shifts the $\nu(\text{C}=\text{O})$ peak at 1718cm^{-1} to longer wavenumber. This represents the consumption of C=C bonds and the loss of conjugation with the C=C bond in the methacrylate hybrimer due to photo-polymerization in the initial stages of UV illumination. However, it may be seen that the integrated area of the $\nu(\text{C}=\text{O})$ band at 1718cm^{-1} remains constant. The degree of conversion of the C=C bond was calculated

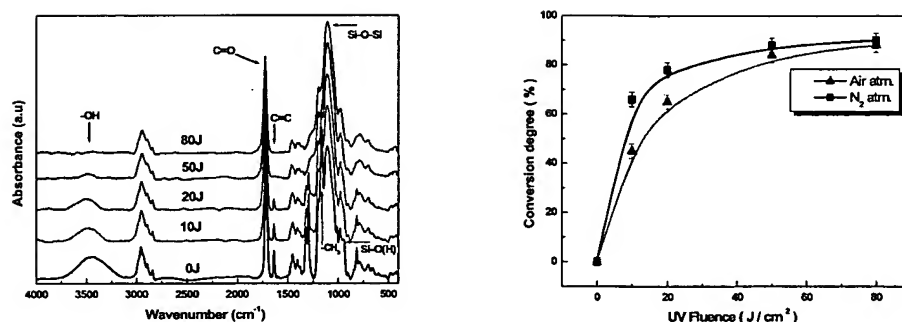


Figure 2. Photo-polymerization behavior of Ge-doped methacrylate hybrimer with a photo-initiator under illumination of a Hg/Xe lamp (220–260nm) (a) FT-IR spectra and (b) Calculated degree of conversion of the C=C bond as a function of UV fluence in air and in a N₂ atmosphere.

by the ratio of the integrated area of the $\nu(\text{C}=\text{C})$ peak to the integrated area of the $\nu(\text{C}=\text{O})$ peak. We calculated and plotted this as a function of UV fluence as shown in Fig. 2(b). The degree of conversion of the C=C bond increases up to 90% with growing UV fluence. This indicates photo-polymerization occurs efficiently in the hybrimer under illumination with light of short UV wavelength. In addition, the intensities of the $\nu(\text{Si}-\text{O}(\text{H}))$ peak and the $\nu(-\text{OH}$ stretching mode) band around at 944cm^{-1} and at 3400cm^{-1} respectively, and the $\nu(-\text{CH}_3)$ peak at 1166cm^{-1} gradually decrease with fluence. This indicates that a concurrent photo-induced condensation between silanol and alkoxy in the meta-stable siloxane network occurs during illumination with UV light. Therefore, sharp changes in the refractive index and the film thickness in the initial stage of

exposure to UV light (Fig. 1(a)) are attributed to structural densification caused by the photo-polymerization of methacrylates and the photo-induced condensation of siloxane.

Fig.3 shows the FT-IR spectra of the films and the degree conversion of the C=C bond as a function of fluence, this time under illumination from the Hg lamp. The intensity of the $\nu(\text{C}=\text{C})$ peak at 1638cm^{-1} barely decreases, resulting in a low degree of conversion of less than 10%. This indicates that the photo-polymerization is not induced by irradi-

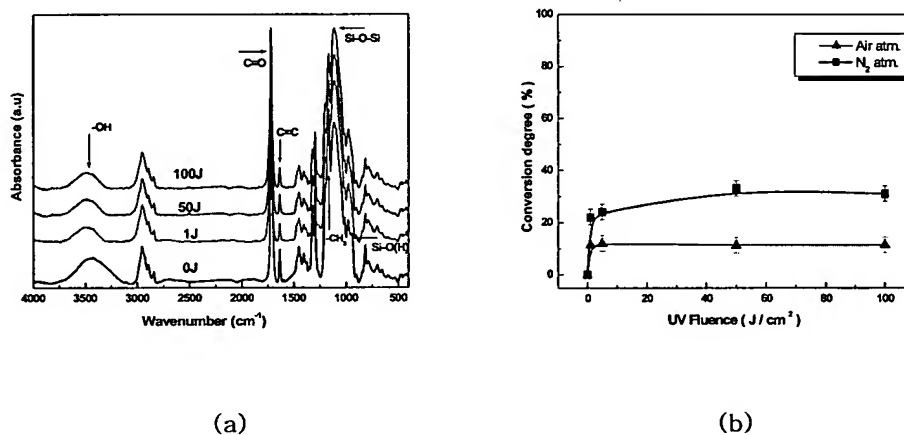


Figure 3. Photo-polymerization behavior of Ge-doped methacrylate hybrimer with a photo-initiator under illumination of a Hg lamp (350-390nm) (a) FT-IR spectra and (b) Calculated degree of conversion of the C=C bond as a function of UV fluence in air and in a N_2 atmosphere.

ation with light from the long UV wavelength part of the spectrum. Also, no significant change in the intensities of the $\nu(\text{Si-O(H)})$ peak, the $\nu(-\text{OH}$ stretching mode) band, the $\nu(-\text{CH}_3)$ peak is seen during the illumination. This indicates that light with a long UV

wavelength does not induce the condensation reaction. Thus, almost no photosensitivity is observed under illumination with the Hg lamp except a very small change in the first stage of irradiation as shown in Fig. 1(b).

Oxygen inhibition has always been a problem in the free-radical photopolymerization of acrylates. The presence of molecular oxygen strongly influences free-radical polymerization because the free radicals formed by the photolysis of the initiator are rapidly consumed by O_2 molecules to yield peroxy radicals.^[23,24] These species are not reactive towards the remaining unreacted monomer and can therefore not initiate or participate in any polymerization reaction. This detrimental effect of oxygen is also suspected to have a pronounced influence on the free-radical photopolymerization of the Ge-doped methacrylate hybriimer. To investigate this, the films were irradiated using the Hg/Xe lamp and the Hg lamp in an N_2 atmosphere. Fig. 2(b) shows the results of the degree conversion of the acrylic double bond as a function of UV fluence for irradiations performed in N_2 and in air. The variation of the degree of conversion with increasing fluence in the case of the Hg/Xe lamp is almost identical in air and N_2 atmosphere. On the other hand, exposure to the Hg lamp in N_2 atmosphere raises the maximum value of the degree of conversion compared to that in air as shown in Fig. 3(b). Therefore, the illumination with long wavelength UV light in an N_2

atmosphere can enhance the photo-polymerization but its effect is small compared with that of employing radiation with a short UV wavelength.

2.2 Photo-polymerization without a photo-initiator

Recently, it was reported that the acrylates, like most other organic compounds, can be photo-polymerized by irradiation with light of short UV wavelength, that is, below 260nm. ^[25, 26] This result is explained by the large absorption at short wavelength and also the high photon energy. Thus, it is expected that the Ge-doped methacrylate hybrimer can be also photo-polymerized to create photosensitivity without adding a photo-initiator. Fig.4 shows the photo-polymerization behavior of the hybrimer without a photo-initiator as a function of the UV wavelength. In the short wavelength region in Fig. 4(a), the intensity of the $\nu(\text{C}=\text{C})$ peak gradually diminishes with increasing the fluence up to $80\text{J}/\text{cm}^2$. This clearly confirms that the excitation of the $\text{C}=\text{C}$ double bonds is caused not by a photo-initiator but the high energy photon itself directly initiates the photo-polymerization of the acrylates in the hybrimer. In other words, the high photon energy can induce photo-polymerization without using a photo-initiator. Thus, li-

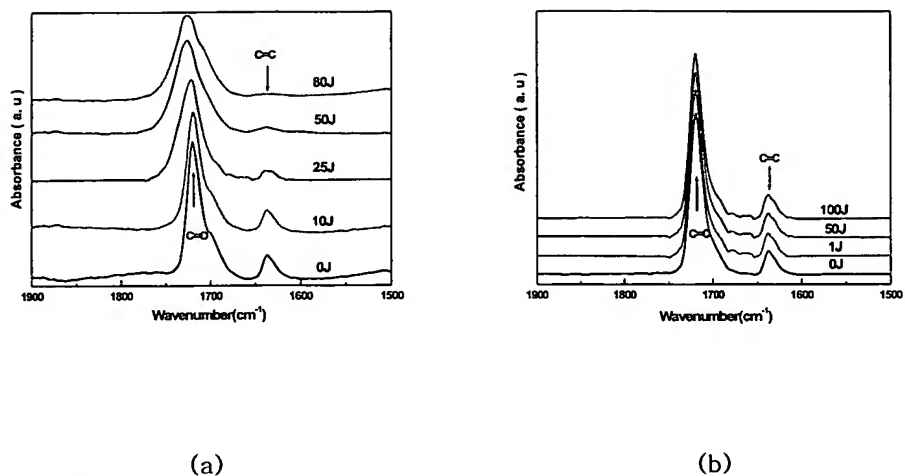


Figure 4. Degree of conversion of the C=C bond in Ge-doped methacrylate hybrimer without a photo-initiator under illumination of (a) a Hg/Xe lamp (220–260nm) and (b) a Hg lamp (350–390nm).

light from the short UV spectrum can photo-polymerize the methacrylate group in the hybrimer even without adding a photo-initiator. As a result, the degrees of conversion in Fig. 2(b) are almost the same even though the illumination is made in an air atmosphere. In contrast, when employing long wavelength light the intensity of the $\nu(\text{C}=\text{C})$ peak in the spectrum from the hybrimer is not changed at all, indicating a very small degree of conversion, as shown in Fig. 4 (b). This explains the reason why the degree of conversion is low at this wavelength even with long exposures as seen in Fig. 3 (b). This shows that photo-polymerization cannot occur without adding a photo-initiator as expected when using light of this wavelength. The methacrylate has no

absorption at this wavelength and the energy of the photon is too low to induce direct excitation of the C=C double bond for the photo-polymerization. An almost constant difference in the degree of conversion of the C=C bond is seen between the results in air and in N₂. The consistently lower value in air is due to the detrimental effect of oxygen. This effect is not seen in the data obtained when using the shorter wavelength illumination as the effect of oxygen is compensated in this case.

2.3 Germanium-related densification

Based on the idea of the photosensitive Ge-doped silica glass, a sol-gel derived Ge-doped methyl hybriimer was examined and showed high photosensitivity, consisting of large changes in its refractive index and an accompanying volume compaction.^[19, 20] This is due to the Ge-related densification of the silica network, which was found only in the Ge-doped hybriimer. The Ge-related densification consists of the compaction of the matrix by the breakage of the Ge-O bond. It was produced in the hybriimer by illumination with light of short wavelength as in the silica glass. It was also found that the photosensitivity was enhanced in the Ge-doped methacrylate hybriimer by the photo-polymerization of methacrylate.^[20, 27] Ge precursor or TMOS are used to prepare Ge-doped or -undoped films respectively and then the photosensitivity of the hybriimer

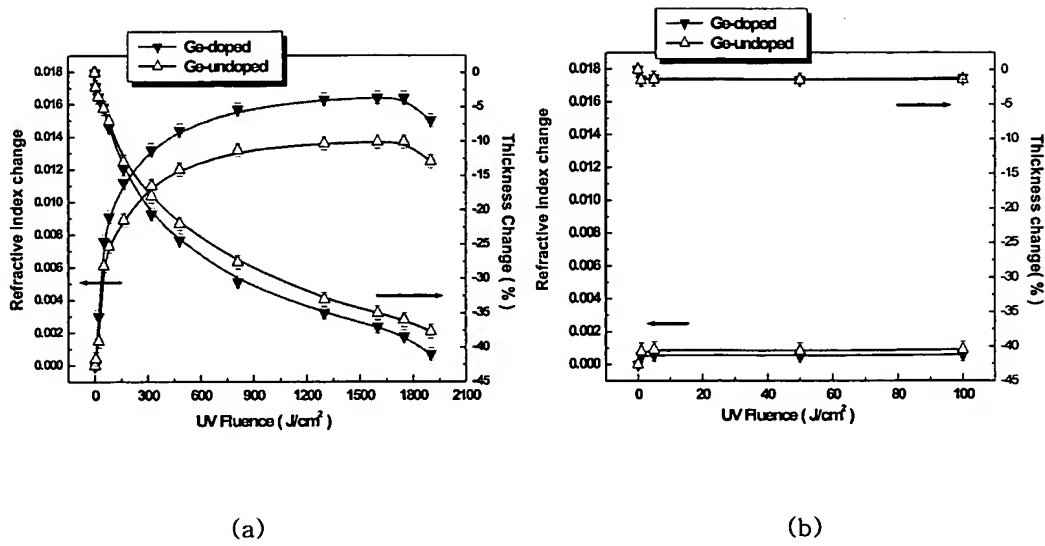


Figure 5. Changes in refractive index and film thickness of Ge-doped and undoped methacrylate hybrimer illuminated by (a) a Hg/Xe lamp (220–260nm) and (b) a Hg lamp (350–390nm) as a function of UV light fluence.

films, Ge-doped or -undoped methacrylate hybrimer, was investigated to examine the role of Ge-related densification. The changes in refractive index and film thickness upon exposure to UV light are presented in Fig. 5. In the case of Hg/Xe lamp exposure, the photosensitivity of the undoped methacrylate hybrimer synthesized using TMOS, instead of GI is lower than that of the Ge-doped methacrylate hybrimer (Fig. 5 (a)). The distinct difference in photosensitivity between the Ge-doped and -undoped methacrylate hybrimers is attributed to the Ge-related densification. In contrast, illumination with the Hg lamp does not change the refractive index or the film thickness in either doped methacrylate hybrimer or the undoped methacrylate hybrimer (Fig. 5

(b)). Thus, it is confirmed that the Ge-related densification in the hybrimer is activated by light from the short wavelength region of the spectrum. Therefore, a large increase in refractive index and concomitant volume compaction can be made by combining photopolymerization and Ge-related densification by illuminating with light from the short UV wavelength region of the spectrum.

2.4 Photo decomposition of methacrylate

Typically, organic polymers are liable to decomposition upon UV illumination. For example, polymethylmethacrylate (PMMA) is decomposed by long exposures with UV radiation of short wavelength since the carbonyl group absorbs UV light in the 190–280nm wavelength region.^[28] Also, the decomposition of the methacrylate group in the hybrimer which results in a reduction in the refractive index and the film thickness has already been noted.^[17] Thus, the Ge-doped methacrylate hybrimer mainly composed of Si-O-Si network with methacryl groups should also be susceptible to the photodecomposition reaction when subjected to long exposures of UV radiation, leading to decreases in refractive index and film thickness. This behavior is consistent with our observations such as the refractive index decrease which occurs eventually after a very long Hg/Xe lamp irradiation (Fig. 1(a)). The photo-decomposition of methacrylate

seems only to be active when illuminating with short wavelength UV radiation. Fig.6 shows the FT-IR spectra showing the change in the carbonyl group in the Ge-doped methacrylate hybrimer irradiated with light from the Hg/Xe lamp and the Hg lamp. A large fluence (over 810J/cm²) of light from the Hg/Xe lamp diminishes the carbonyl $\nu(\text{C=O})$

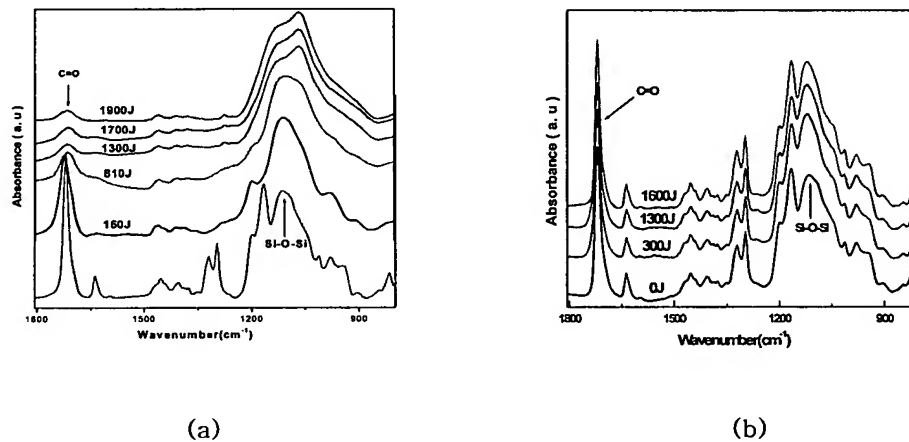


Figure 6. FT-IR spectra of Ge-doped methacrylate hybrimer illuminated by (a) a Hg/Xe lamp (220-260nm) and (b) a Hg lamp (350-390nm) as a function of UV light fluence.

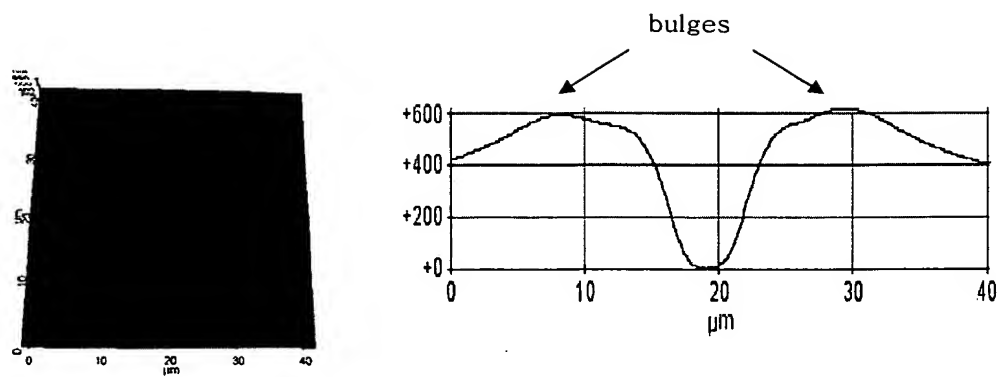
O) stretching mode peak at 1718cm^{-1} continuously as the fluence increases. This confirms the occurrence of the photo-decomposition of the methacrylate in the Ge-doped methacrylate hybrimer (Fig. 6 (a)). During the photo-decomposition of the methacrylate, high index molecular species including polar carbonyl groups are evaporated off as gaseous products decreasing both of the refractive index and the film thickness of the Ge-doped methacrylate hybrimer. In addition, the intensity of the Si-

O-Si peak at 1108cm^{-1} shifts to lower wavenumber indicating the decrease of the Si-O-Si bond angle upon UV light irradiation using the Hg/Xe lamp. This shows that a further densification reaction of the silica network proceeds as the bulky methacrylate chains are removed by the photo-decomposition. The densification can also contribute to the reduction of the film thickness. On the other hand, the carbonyl stretching mode peak is unchanged with Hg lamp irradiation as seen in Fig. 6 (b). This indicates that the methacrylate is not decomposed with long UV wavelength radiation as expected for polymers. Also, no change in the Si-O-Si peak is found in the hybrimer illuminated by the Hg lamp as shown in Fig. 6 (b) and that is because the methacrylate groups stick to the matrix even after a lengthy exposure to UV light.

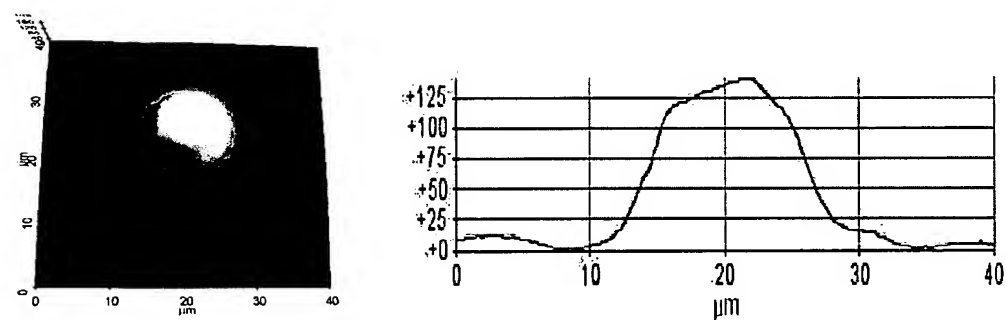
2.5 Direct photo-patterning

The Ge-doped methacrylate hybrimer is directly photo-patternable without any developing step because of simultaneous changes in both the refractive index and the thickness upon exposure to UV light. As shown and discussed above, the hybrimer is photosensitive only with the Hg/Xe lamp which has short wavelength light. The hybrimer is shrunk by photo-polymerization and photo-condensation during the initial stage of UV irradiation (low fluence), and Ge-related densification, photo-

decomposition and silica densification at a later stage of UV irradiation (high fluence). In contrast, only a small amount of photo-polymerization occurs in hybrimers during the initial stages of illumination with an Hg lamp. Thus, it is expected that the shape patterned by direct UV exposure can vary depending on the UV lamps used. Direct photo-patterning was carried out using a UV fluence of $1800\text{J}/\text{cm}^2$ through a quartz contact mask consisting of a single $5\mu\text{m}$ circle using both an Hg/Xe lamp and an Hg lamp. The pre-drying process was employed as is necessary in the use of a contact mask and reported previously.^[13] Fig.7 shows a three-dimensional atomic force microscope (AFM) image of the single circle pattern on the Ge-doped methacrylate films after illumination by the different UV lamps. Lens like shapes may be detected that possess different shapes depending on which lamp was employed. The Hg/Xe lamp exposure makes concave-lens like shapes induced by volume compaction that is due mainly to photo-polymerization and Ge-related densification (Fig. 7(a)) as expected. Surprisingly, a convex-lens like shape is seen after direct photo-patterning using the Hg lamp even though little photo-induced reduction of the film thickness is found in Fig. 1(b). It was found that selective UV light exposure using a photo-mask can be accompanied by mass transport of material via a diffusion process of the monomer and/or small molecular oligomers in the hybrid film.^[29] When UV light was irradiated onto a specific



(a)



(b)

Figure 7. AFM images of the direct photo-patterning of a single circle in Ge-doped methacrylate hybriimer illuminated by (a) a Hg/Xe lamp (220–260nm) and (b) a Hg lamp (350–390nm).

area, the photo-initiator was decomposed and reacted with a polymerizable group. The photo-polymerization takes place only in the illuminated areas, leading to the formation of concentration gradients in the films. Consequently, diffusion of the constituents occurs from the non-irradiated regions to the irradiated regions of the hybrid films,

which results in the creation of volume expansion in the exposed area. This photosensitivity mechanism in the hybrimer is called photo-migration. Thus, the shape resulting from direct photo-patterning by Hg lamp exposure can be convex-lens like due to volume expansion from photo-migration. On the other hand, for the illumination with the Hg/Xe lamp, photo-migration is dominated by the other major photosensitive mechanisms revealed in this study. This results in direct photo-patterning of a concave-lens like shape. However, the bulges at the edge of the shape as shown in Fig. 7(a) are due to the occurrence of photo-migration from the Hg/Xe lamp exposure. Therefore, the Ge-doped methacrylate hybrimer is a potential photosensitive material to be use in the fabrication of various shapes for micro-optical devices. The appearance of the micro-optical structures can be controlled by changing the wavelength of the UV light and its fluence.

3. Conclusions

The Ge-doped methacrylate hybrimer showed different photosensitivity depending on the wavelength of the illuminating light. Under illumination with 220–260nm wavelength light, the hybrimer undergoes photo-polymerization, photo-condensation, germanium-related densification, methacrylate decomposition and silica network densification.

Specifically, as for photo-polymerization, the hybrimer is photo-polymerized by the energetic photon without adding a photo-initiator. As a result, the short wavelength illumination creates high photosensitivity, consisting of large changes in refractive index and film thickness. On the other hand, under illumination with light of 350–390 nm wavelength, the hybrimer exhibits negligible photosensitivity and photo-polymerization occurs only by photo-initiator. Photosensitivity to long wavelength UV light can be enhanced by irradiation in N₂ atmosphere, but the response is much lower than to UV light with a short wavelength.

The shapes obtained from the direct photo-patterning on the Ge-doped methacrylate hybrimer were also dependent on the wavelength of the UV light. The short wavelength light produced concave shapes mainly due to the photo-polymerization and the Ge-related densification. On the other hand, the convex shape is fabricated by long wavelength UV light irradiation since only photo-migration occurs from unexposed areas to exposed areas without any densification.

4. Experimental

Ge-doped methacrylate hybrimer was prepared from 3-trimethoxysilylpropyl methacrylate (MPTS, Aldrich) and germanium isopropoxide (GI, Aldrich) with 9:1 molar

ratio. Since the hydrolysis reaction of Gl was very fast compared with that of MPTS, MPTS was first hydrolyzed with 0.75 equivalents of water in the presence of 0.01N hydrochloric acid (HCl) as a catalyst. After that, Gl was added to the prehydrolyzed solution and stirred for 1 hour to advance the hydrolysis and the condensation. The mixed solution was reacted with additional water for 24 hours to complete the hydrolysis and the condensation. The total amount of water used was 2.625 mole % over total silane in the solution. The obtained solution was totally transparent. 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-11(Irgacure369, Aldrich) was added to the transparent solution as a photo-initiator of the methacrylate. Subsequently, the transparent solution was filtered through a 0.22- μm filter to remove impurities and bubbles. The solution was then coated onto a p-type Si (100) wafer by spin coating at 4000rpm for 30s. Single coating yields an approximate film thickness of 5-6 μm . The films were illuminated by a Hg/Xe lamp (Oriel 82511, power density of $70\text{mW}/\text{cm}^2$ with spectral ranges of around 220-260nm) and a Hg lamp (Oriel 97435, power density of $70\text{mW}/\text{cm}^2$ with spectral ranges of around 350-390nm).^[30]

The molecular structural change of the films upon UV light illumination was investigated by Fourier transform infrared (FT-IR, JASCO 680 Plus) spectroscopy. The refractive index and thickness of the films were measured at 632.8nm with a prism

coupler (Metricon 2010). Direct-patterning of the Ge-doped methacrylate hybrimer was carried out using an ultraviolet light fluence of 1800 J/cm^2 through a quartz contact mask. Finally, the patterned micro-images were observed with an Atomic Force Microscope. (AFM, Park Scientific Instruments, Auto probe 5M)

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